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NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

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No. 548

CONTRIBUTION TO THE STUDY OF NORMAL BURNING
IN GASEOUS CARBURETED MIXTURES

By M. R. Duchêne

PART II

From Service Technique et Industriel de l'Aéronautique
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C O N T E N T S

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NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS.

TECHNICAL MEMORANDUM NO. 548.

CONTRIBUTION TO THE STUDY OF NORMAL BURNING
IN GASEOUS CARBURETED MIXTURES.*

By M. R. Duchene.

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of the French Air Ministry and the author.)

PART II.

Chapter III.

Experimental Results

12. General Aspect of the Explosive Process.— All of the photographic figures obtained have the general characteristics of Figure 11.

It is to be noticed that the flame front propagates itself at variable velocity from one end of the tube to the other. At the start the velocity is not null but is accelerated for some thousandths of a second (405 for hydrocarbons of C_6). At the point where the curve makes its first inflection, the velocity is maximum. At this point the velocity decreases rapidly to reach its minimum. There then follows a second point of inflection. The velocity then increases slowly till it has reached the extremity of the tube.

The combustion is not terminated at this instant but incandescence continues in the tube for a period about equal to that

*From Service Technique et Industriel de l'Aéronautique, Bulletin Technique No. 54, December, 1928. For Part I, see Technical Memorandum No. 547.

required for the flame to traverse the tube. If the intensity of luminescence on the film is comparable to the intensity of chemical reaction, it would indicate that the processes of combustion taking place after the flame had traversed the tube was more important than the combustion connected with the propagation of the flame.

13. The Measure of Velocity.-- The rate of displacement of the photographic film may be accurately known (See Section 11, Part I - N.A.C.A. Technical Memorandum No. 547, page 17) and the opaque strips placed two centimeters apart along the tube serve to determine the distance traversed by the flame front.

In order to increase the precision of measurement, we have drawn a pantograph of each photographic figure. From the curves so obtained we have measured the differences of the ordinates Δe , corresponding to the differences of the abscissas Δt , and have taken for the velocity over the period $t + \frac{\Delta t}{2}$ the value of $\frac{\Delta e}{\Delta t}$. Δt was taken equal to $\frac{1}{2000}$ second.

14. Influence of the Ignition Spark.-- The electrical energy liberated by the spark has an influence on the propagation of the reaction area.

The following influences have been observed:

1. On the lower limit of inflammability as shown by the table given below.

Hydrocarbon	Length of Spark Gap	
	15 mm	6 mm
	c_{\min} for flame propagation	No propagation for $c =$
Cyclohexene C_6H_{10}	8.2	10.2
Hexane C_6H_{14}	6.4	8.5

The spark is usually designated by the length of gap; but in all cases for this study the length of gap was about 1 mm.

The indicated concentration is given by the expression $c = 100 \times \frac{\text{hydrocarbon}}{\text{air}}$ by weight.

2. By the darkening of the photographic plate. This takes place progressively in the first case (Fig. 12) and takes place abruptly in the second case (Fig. 12₂).

In the second case (Fig. 12₂) the flame is extremely weak in actinic quality at first and at the second point of inflection becomes brusquely very actinic, and this quality extends into the gases that have already been traversed by the flame area. From this it seems probable that the first reaction is succeeded by a second of quite different nature, for which the first served only as a preliminary.

Although the spark characteristic in this case corresponds to a maximum explosive distance greater than 10 mm at atmospheric pressure, the propagation developed by it always corresponds to that given by a spark of 15 mm maximum explosive distance; that is, to say, it follows the mode shown by Figure 12₂.

15. Influence of Mixture Ratio on Flame Velocity.— Two sets of observations made under conditions somewhat different were carried out. The records are designated set A and set B. There are shown below by coordinate figures the curves for flame velocities of the reaction expressed as functions of time and mixture ratio.

Experimental Conditions

	A	B
Dimensions of explosive tube (Fig. 9)	{ length 85.5 mm diam. 23.5 "	length 109 mm diam. 23 "
Volume of tube	37.0 cm ³	43 cm ³
Ratio of compression r at ignition	4.2	4.4
Initial temperature (before compression)	85°C	85°C
Spark characteristic (length of gap)	6 mm	15 mm

16. Benzene, C_6H_6 $d_{18} = 0.880$ (Fig. 13) - Experimental Conditions, A.— The numbers given the curves in the figure refer to the mixture ratio, $c = 100 \frac{\text{hydrocarbon}}{\text{air}}$ expressed in terms of mass.

For $c = 7.5$ the photographic record was very weak. Results from this record are not shown in Figure 13. There was no luminosity of the gases after the passage of the flame.

For those concentrations whose curves are given in the figure, luminosity was present in all cases after the flame had passed. The intensity of the luminous effect increased progress-

ively and reached its maximum after the flame had traversed the tube.

The time required for the flame to traverse the tube is given by the graph. It may be seen that this period is the greatest for $c = 8.9$ and $c = 21$; that is to say, for the richest and poorest mixture ratios observed. For $c = 15.6$ the flame velocity is greatest and the time required to traverse the tube the least.

The duration of luminosity in the tube varies from 26 to 29 thousandths second.

17. Cyclohexane, C_6H_{12} $d_0 = 0.809$ (Fig. 14) - Experimental Conditions, A.- In general, the actinic properties of the flame in this reaction are feeble at first, then abruptly become intense, following the order shown in Figure 12₂.

It is also to be noted that a maximum velocity occurs for $c = 15.6$ the same as for benzene, C_6H_6 .

The velocity shows a decrease for weak as well as for rich mixture ratios.

The duration of the luminous effect varies between 22 and 30 thousandths second - similar to that of benzene.

18. Cyclohexane, C_6H_{12} (Fig. 15) - Experimental Conditions, B.- The mixture ratio $c = 7.2$ gives a faintly luminous reaction. For still lower mixture ratios a traceable photograph was not secured.

In this series of experiments we did not go above the mixture ratio $c = 14$; but it is evident this number is still below that for maximum velocity.

Under these experimental conditions, and contrary to the results observed under conditions A, the darkening of the photographic figures was gradual and progressive (See Section 14: Influence of the Ignition Spark, page 2).

19. Cyclohexene, C_6H_{10} $d_0 = 0.8089$ (Fig. 16) - Experimental Conditions, A (defined above). - Maximum velocity was obtained for $c = 17.7$.

As was observed for cyclohexane, the darkening of the photograph is in this case also abrupt. It presents the appearance shown in Figure 12_a.

Some of the photographs show clearly a propagation by reflection following the passage of the flame through the tube. Two successive reflections in contrary sense are distinguishable (See Plate I, photograph 1).

From this it may be supposed that the luminosity that develops after the passage of the flame is the result of successive propagations, first in one direction, then in the other, in the course of which the combustion is completed.

The duration of luminosity in this case is between 28 and 37 thousandths of a second

20.- Cyclohexene, C_6H_{10} (Fig. 17) - Experimental Conditions,

B. (defined above).-- When under the experimental conditions A a propagation will not develop below the mixture ratio $c = 11.5$, under conditions B it is found that a propagation occurs for a mixture ratio $c = 8.2$.

This difference may be explained by the difference in energy of the electric spark in the two cases (See Section 14, page 2).

The curve drawn for the mixture ratio 12.3 in Figure 17, corresponds only to the upper limit of inflammability.

21. Hexane, C_6H_{14} $d_{17} = 0.663$ - Experimental Conditions, ..

A.-- A graph similar to the ones above given will not be attempted for the reaction of this fuel; the reason is because the flame is too weak in actinic properties to give a record sufficiently definite for accurate measurement. There will be found in the table that follows, however, some values that could be determined.

The photographs, excepting the first, are of a type given by Figure 12₂ - the region where darkening of the plate occurs is abrupt.

The propagations following the first passage of the flame are well marked although the first propagation was so pale (Plate I, photograph 3).

The decrease in the limits of ignition is due to the weak energy of the ignition spark.*

*The experimental results found for this case seem to confirm the observations of W. M. Thornton (Proc. R. S. London, 1914, 90, 297) who connected the shortening of the limits of inflammability of methane and some other hydrocarbons with a decrease of current in the primary of the induction coil producing the spark.

Mix- tur ratio C%	Duration of combustion in sec/1000		V e l o c i t y m/sec.				Remarks
	luminous	flame	After $\frac{2}{1000}$ sec.	maxima	minima	Mean velocity	Compres- sion ratio 4.2
6.3							No flame
8.5							No flame
8.7	26 to 27	12.5	6.8	10.1	4.4	6.1	Progressive luminosity
10.7	30	16.0	4.6	8.3	2.7	4.8	1st passage, flame pale. 2d passage, echo lumi- nous. 3d passage, echo less luminous.
11.6	25	14.5	4.6	8.0	2.7	5.3	Flame very pale, fol- lowed by increase in luminos- ity.
13.1							No flame

22. Hexane, C_6H_{14} - Experimental Conditions, B (defined above). - For these experimental conditions the limits of propagation are much better marked and it was possible to obtain a curve of speeds for the mixture ratio, $c = 6.4$.

From the graph above given (Fig. 18), it may be seen that the speeds of propagation constantly increase with increasing

values of c . In the other figures given, the speeds at first increase with increasing values of c until a maximum is reached, when further increase of c produces a decrease in speed.

For the mixture ratio $c = 9.5$, the following facts may be observed:

(a) With a mixture ratio $c = 10.1$, the impression on the film is much paler than that from $c = 8.4$ or from $c = 9.5$ although the violence of the explosion is no less (as estimated by the rebound of the ram) than in the other cases. The curves representing the displacement of the flame front in time are in all respects the same as for the mixture ratio $c = 8.4$.

(b) With a mixture ratio $c = 12.8$, no darkening of the photographic plate is appreciable and there is no perceptible trace of the propagation of the flame though in this case also the violence of the reaction is not less than that for $c = 10.1$. C.R. 187, 200, (1928).

There is then in this case a violent explosive reaction yielding no photographically active rays. We shall revert to this subject in a later chapter.

24. Influence of Initial Temperature.— Investigations of the effect of initial temperature on the reaction were made with benzene and with hexane. For the first-named of these hydrocarbons there is given below a table by which the effect of an initial temperature, 55°C , 70°C , and 85°C , on the reaction of

this fuel may be made. For the case of hexane the results are given in graphic form in Figure 19. Temperatures are indicated on the curves. The experimental conditions for these reactions were those designated B.

Initial temp. before compression	Duration in $\frac{\text{sec.}}{1000}$		Velocity in meters per second			R e m a r k s c = 14, r = 5 Tube volume 37 cm ³
	total	flame	maxima	minima	mean	
17°C		33			2	Propagation only slightly luminous.
40	41	17.7	7.0	1.5	3.80	Photographic record well defined. Darkening of plate progressive
55	31	11.1	12.0	4.0	6.00	
70	28	11.3	12.5	2.5	6.00	
85	32	11.1		2.5	6.00	For reproduction of these photographs, see Plate II

From the above table, it is to be noted that:

1. The propagation is established with difficulty at ordinary temperature, and that its rate of progress is slow.
2. That the velocity of propagation increases with increase of initial temperature but that the rate of increase with temperature decreases rapidly.

Between 55°C and 85°C, initial temperature of the mixture not much difference in effect is noticeable.

For the other fuel, hexane, whose results are shown graphically in Figure 19, no distinguishable variation in velocity is noticeable for variations in initial temperature. The mean ve-

locities required for the passage of the flame in the tube remain the same. It is also to be noticed that for each temperature the maximum velocity acquired is also the same.

The period required for attainment of maximum velocity seems to decrease with increasing initial temperature. In a following chapter an explanation of this phenomenon is offered.

25. Influence of Degree of Compression.-- In the apparatus used in these studies, the final volume of the reacting gaseous mixture remains constant v . The initial volume, however, is variable.

There is given in Figure 20, a graphical resume of results obtained from different initial compression ratios. The fuel used was cyclohexane, C_6H_{12} .

An increase in compression ratio

1st, diminishes the time necessary for the flame to traverse the tube. In other words, it increases the mean velocity.

2d, it increases the value of the maximum velocity and decreases somewhat the period required for its attainment.

There were other observations made with hexane; the results confirmed the above statement.

Degree of compression r	Duration in sec/1000		Velocity meters per second		
	total	flame	maxima	minima	mean
3.1	30	12.5	8.9	1.8	6.1
5.1	25	10.7	10.5	2.3	7.2

26. Influence of Tetraethyl-Lead.— The effect of tetraethyl-lead was first observed on a discontinuous type of propagation like that shown in Figure 12₂; that is to say, in a propagation characterized by an abrupt increase in the actinic qualities of the flame.

For these observations, mixtures of cyclohexane and ethyl-lead were made up containing 1 and 2% ethyl (by volume) in the mixture. Plate III is a reproduction of the two photographs obtained. It is to be observed that the development of abrupt luminosity is less and less pronounced as the amount of ethyl is increased. (C.R. Ac. Sc. 186, 220 (1928) .) This characteristic, shown by the photographs, leads one to think that the effect of an anti-detonator is to render the successive phases of an explosive reaction less abrupt.

On the other hand, we have been able to show that when the experimental conditions B were imposed on the reaction of mixtures of ethyl and hexane (mixture ratios of hexane and air, $c = 12.8$) all trace of the propagation disappeared from the photographic plate although the explosion took place with a violence certainly equal to those giving a well-marked trace.

The addition of 5% of the ethyl lead to the mixture brought back a photographic figure on the plate. (C.R. Ac. Sc. 187, 200, (1928).) If the disappearance of a trace of propagation from the photographic plate was due to the establishment of the detonation wave (This assumption seems justifiable from the work of Henne

and Clark, "Spectographie de flammes dans un moteur a explosion," C.R. Ac. Sc. 184, 1927), then the reappearance of the image following the addition of more ethyl-lead might be taken to mean that the addition of the anti-detonator prevented the development of detonation.

Figure 20' permits a comparison of the actinic properties of the flame with and without an anti-detonator present in the mixture.

27. Influence of Length of Explosion Tube.— The influence of the length of the tube seems to affect the duration of time necessary to develop maximum velocity. The shorter the tube, the shorter the time required to reach maximum velocity.

This may be observed in the graphic figures (14 and 15), for the case of cyclohexane, and Figures 16 and 17 for the case of cyclohexene.

A discussion of this phenomenon will be taken up in the following chapter.

28. Remarks.— In the course of the experimental work it was noticed quite accidentally but in a number of cases, that if a succession of sparks followed the ignition of the mixture — the flame having in the meantime traversed only a fraction of the length of the tube — that the rate of propagation was retarded. The rate of propagation is evidently the same at the beginning in both cases, but it seems that the succession of sparks following that producing ignition, have the effect of

prolonging the period of minimum velocity. The curve here runs nearly parallel with the edge of the film for a longer time when the sparks are continuous than when only one ignition spark passes, and this period is longer, the longer the sparks are continued. This retardation, which amounts practically to an arrest of the flame, continues from one to two hundredths of a second or during the interval of three successive sparks at intervals of 0.004 second.

Chapter IV

Discussion of Preceding Results

29. General Aspect of the Figures.— The questions may arise if the undulatory form of the flame trace may not be due to purely accidental causes. In other words, if it may not depend on the way compression and ignition are brought about in the gaseous mixture, or perhaps by the rebound of the piston and the effect this succession of events may have on the reaction process.

The period occupied by the piston in coming to rest is generally much greater than the period occupied by the flame in traversing the tube. The time occupied by the piston in coming to rest for those cases where the reaction is quickest, is $1/50$ second, while the period required for the passage of the flame is shorter, being about $8/500$ second.

The experimental arrangement made use of in making these determinations consists of a device by which the ram producing com-

pression closes an electric circuit as the piston reaches its seating. The instant of closing the circuit is registered on a revolving drum on which is registered at the same time the trace of a calibrated tuning fork.

As still further proof, we give the reproduction of a photograph obtained in the course of our experiments where the glass tube broke before the piston and ram rebounded. It may be seen that the flame not only had time to traverse the tube but that the tube remained illuminated for a number of thousandths second. (Plate IV).

In order to determine the effect of the impact of the ram on the piston, a number of exposures were made of the reaction when the piston was pushed home without impact. These latter records were not distinguishable from those where the falling ram was used.

Since the ignition spark is induced by the ram as it drives the piston home, ignition takes place an instant before maximum compression is reached. In other words, we can say "The spark is slightly advanced." Usually ignition took place an instant after maximum compression. In general, no change in results were noted.

It is evident, from what has been stated above, that in reference to the time of arrest of the piston, the effect of rebound of the compression system after the reaction has no effect on the photographic records secured. The piston has also been

prevented from rebounding without showing any change in the photographic image.

The characteristics exhibited by the course of the flame trace are then the characteristics due to the course taken by normal burning induced in a short closed tube under the conditions that have been described.

It was pointed out in Chapter I (See N.A.C.A. Technical Memorandum No. 547 - Part I of this paper) that Le Chatelier found that if the ignition took place at the closed end of a tube open at the other end, the rate of propagation in such a case was continually accelerated. Our observation of the flame movement, started at the end of a closed tube, confirms his observation of the propagation when first started, but in the arrangement employed by us the rate of acceleration rapidly diminishes due to the opposite closed end of the tube against which an impulse is reflected.

Jouguet wished us to state his conception of the processes taking place under the conditions imposed on the reaction by our experimental device. This we are glad to do.

From observations made of explosions in mines (by Taffenel), it is found that all explosions which we have designated as normal burning, are preceded by an impulse wave purely mechanical in its nature. This disturbance has been given the appellation "chasse préalable" (Jouguet, "Mechanique des Explosifs.")

This impulse wave originating in our glass tube by the ignition of the explosive gases, propagates itself through the mixture ahead of the flame by a wave surface CD at the velocity of sound in the gases (Fig. 21,a). However, in this case it does not give rise to a vibratory movement of the gases but propagates itself simply as an impulse wave similar to that formed when a stone is dropped into a body of water at rest.

Figure 21,b illustrates, for a given case, the law governing the velocity of these waves.

The velocity is small for such a compression CD, near the surface of the flame and in consequence its position on the curve PN, will lie close to the x-axis of the figure. It will only be in the neighborhood of the point N that the wave becomes well defined.

The flame advances at a rate of only a few meters per second. The impulse CD advances with a velocity of the order of 350 meters per second. The distance AC, then increases with time.

If the tube is closed at the end toward which the impulse is advancing, the impulse is reflected from this obstruction and disturbs the propagation of the flame. In the actual experimental case considered, this impulse would have time to be reflected back and forth twenty-five times while the flame was traversing the tube once.

During the initial instants of propagation these reflected

impulses modify the medium in which the flame is passing only to a small extent (since the velocity is small in the neighborhood of CD). In the neighborhood of the flame and immediately before it there is a building up of these impulses and in consequence, an increase of velocity relative to the flame front. This explains the acceleration observed in the flame speed.

When the zone NP, preceding the flame front, reaches the closed end of the tube it is reflected, its sign is changed, and its effect is to retard the apparent speed of the flame. This explains the diminution observed in the velocity of the flame.

Then follows, as a result of successive reflections, an equalization of the initial pressure differences set up in the tube, the velocity of the flame becomes more uniform or at least varies more uniformly, as may be noticed in the figures near the termination of the reaction.

30. The Reaction Takes Place by Successive Phases.— It has been pointed out in a preceding chapter, (Section 14, page 2), that there have been obtained under certain experimental conditions, photographic records where a feeble actinic flame quality was abruptly succeeded by a flame quality intensely actinic. It was suggested that this abrupt change in the quality of the flame might be due to a change in the chemical process. If the change was due only to a quantitative change in the same chemical reaction, it does not seem probable that the change would take place abruptly.

The different passages of the flame within the tube first in one direction, then in another, that were noted in the experimental results with cyclohexane and hexane under experimental conditions A, with spark of weak energy - May they not correspond to separate intermediate phases of the chemical reaction?

In support of this point of view it is to be mentioned that various investigators have reported the occurrence of products of intermediate reactions in the case of slow combustion of hydrocarbons. For instance, Callendar (Engineering, 223, 147, 182, 210, 1927) found on submitting hexane to slow combustion, that various aldehydes were formed in abundance.

According to Bone, any hydrocarbon submitted to the process of slow combustion exhibits a tendency to transform its H atoms into groups of OH molecules with the liberation of energy. This is the theory of hydroxylation that seems well confirmed by the recent work of Landa (C.R. Ac. Sc., February 27, 1928).

The formation of intermediate products in the course of the reaction would appear from the point of view of atomic physics, infinitely more reasonable than the direct formation of CO_2 and H_2O which would necessitate an extraordinary coincidence of definite atomic impacts. - in the case of the combustion of benzene the simultaneous meeting of 17 molecules if the reaction took place directly between the initial molecules and the formation of CO_2 and H_2O .

31. Explosive Limits.— In the results given in the preceding chapter the richness of the mixture ratios $c = \frac{\text{hydrocarbon}}{\text{air}}$, has been progressively reduced till no flame trace appeared on the photographic plate.

The curves showing the propagation of the flame for the least mixture ratios (Figs. 13, 15, 17 and 18) were obtained for mixture ratios only a little greater than those that gave no photographic record.

It could be assumed for the cases giving no actinic radiation that there was no flame propagation. If there was an explosion, it would produce a mechanical effect (the piston would rebound further than for a charge of noncarbureted air). Now, for all of these weak mixture ratios that gave no photographic record, there was observed no corresponding mechanical effect on the piston. We conclude, then, that there was no explosion in those cases giving no photographic record.

Now the richness of these mixture ratios is relatively great since they lie near the theoretical chemical ratio for complete combustion; they are all greater than the inferior limits given by other authors.

There is given in the table that follows, in one column the hydrocarbon, in the other its proportion in the chemical equation for complete combustion, and in the third the lower limit of propagation as observed.

Hydrocarbon	Composition of Fuel by weight corresponding to Chemical Equation	Inferior Limit (observed)
C_6H_6	7.6%	$6.9 < c \leq 7.5$
C_6H_{12}	6.5	$6.7 < c \leq 7.2$
C_6H_{10}	6.7	$7.6 < c \leq 8.2$
C_6H_{14}	6.3	$5.9 < c \leq 6.4$

If the performance of a gas engine be calculated from these figures (the cylinder bore and r.p.m. being known), a figure is obtained that is notably higher than that corresponding to the actual working of the engine. The explosions in the cylinder of the engine occur for weaker mixture ratios than the figures given above would indicate.

But it should be borne in mind that the explosive mixture in the engine cylinder is not homogeneous. Suspended in the mixture are globules of liquid fuel. The conditions existing within the cylinder of the actual engine are different from those under which our observations were made.

According to investigations made by Pignot (Bulletin Technique de l'Aeronautique No. 34, Mag. 1926) auto-ignition by adiabatic compression takes place with even weaker mixtures. In this case, however, it is easy to conceive that the energy necessary to maintain propagation would be less than in the other cases because the entire charge is brought to a temperature very nearly that of ignition.

32. Normal Burning and Detonation.— There was stated in Section 3 (See N.A.C.A. Technical Memorandum No. 547 - Part I of this paper, page 10) the hypothesis that the explosive wave develops when coincidence exists at all points in the explosive mixture between the zone of chemical reaction and the mechanical impact wave (between the impact wave and combustion). On this hypothesis analytical formulas have been deduced that give results in remarkable agreement with results experimentally obtained by Vieille, Le Chatelier and Dixon. (Jouguet, "Mechanique des Explosifs," p. 333.)

It seems logical to assume that the explosive wave is a limiting condition, and that there should be found every order of impact wave propagated ahead of the wave of chemical reaction, the flame.

The first action, in fact, occurs at the moment a certain amount of energy is liberated and this participates in the chemical reaction induced. This in its turn has a modifying influence on the process following. For each degree of these two initial processes there will result different initial ignition processes.

The more intense the impact wave the higher will be the temperature induced in it and the more important will be the first chemical reaction induced. The succeeding flame is of less importance in proportion as its reaction energy is of less importance than the energy of the impact wave.

A complete reaction due to the passage of an impact wave constitutes an explosive wave leaving no flame behind it.

These considerations seem to be supported by our experiments with hexane rendered more and more rich. It was shown that with a mixture ratio 8.4, there was obtained a well-marked photographic record; with a mixture ratio 10.1, the record was pale but the mechanical effect of the explosion was not lessened; with a mixture ratio 12.8, the record was not distinguishable although the violence of the explosion was apparently the same.

Henne and Clark (C.R. Ac. Sc. 184) have reported that they obtained from an explosive wave in a cylinder, ultra-violet rays extending to 2360 Å, while from ordinary normal burning they could secure them only to 3400 Å.

It seems/^{then}that the weakness of a photographic impression might be attributed to detonation - the glass of our tube and lens system arresting the ultra-violet rays.

The first photographic impression cited above would then correspond to normal burning; the second to a normal burning much attenuated by the passage of an intense impact wave in front of the flame; the third case to detonation.

33. Role of Anti-Detonants.— The effect of tetraethyl-lead is to confine the luminous radiations to the range of the visible spectrum as indicated in Section 26. If the hypothesis stated above concerning the effect of anti-detonants, is accepted, then

it appears that their effect is to retard the chemical action due to the impact wave that precedes the flame.

It has also been noted that the effect of anti-detonators is to oppose abrupt changes in the reaction. It is interesting to compare the results given in Section 26 and shown in Plate III, with results obtained recently by Callendar (Engineering, February 4, 1927, p. 147). He attributes the development of the explosive wave to the formation of peroxides that decompose with violence. According to this author, the presence of an anti-detonator prevents the formation of these peroxides.

34. Remarks on the Existence of "la chasse prealable."— It was stated in Section 27 that maximum velocity was reached at the end of a longer period in a long tube than it was in a short tube.

If "la chasse prealable" is in reality the cause of the retardation of the accelerating velocity, then it is reasonable that it should produce its retardation later in a long tube than in a short one, since in a long tube it would have further to go. This conclusion is in accord with observation.

It has also been pointed out that maximum velocity is attained the quicker the higher the initial temperature.

The "chasse prealable" that is assumed to cause the arrest of acceleration propagates itself then more rapidly in a mixture of high temperature than in a mixture at low temperature. If the "chasse" is indeed a mechanical impulse then it should propagate itself the more rapidly in a warm medium, as in the case with sound.

Chapter V

An Analytical Study of Propagation in a
Combustible Mixture Confined in a Closed Tube

35. Hypotheses.— Consider a cylinder closed at its two extremities and containing an explosive ignited at one end.

We will carry out the proposed analysis in the way already adopted by Mache (Die Physik der Verbrennungerscheinungen, Leipzig, 1918) in his study of the propagation within a sphere fired at the center.

Suppose the propagation to proceed by thin sections perpendicular to the axis of the cylinder. The propagation takes place in such a way that there is no heat exchange from one section to the other^{*}; neither between the burned gases and the gases not burned, nor between the gas and the walls of the container.

The pressures are assumed to equalize themselves instantly.

The sections burned are not at the same temperature. This assumption is rational since a section taken anywhere in the initial gases will be compressed at the moment of combustion. The

^{*}This hypothesis, which is made to simplify calculations, would seem to be in contradiction to the statement made concerning normal burning in Section 4 (See N.A.C.A. Technical Memorandum No. 547 - Part I of this paper, page 10); the transmission of heat from one section to the other contributes, in fact, to the propagation but increase of temperature due to compression, takes place, nevertheless.

more it has been compressed the more its temperature will be raised by its combustion. In return, all the burned gases are at the same temperature.

It is further assumed that there is no turbulence, no dissociation, and that the consideration is confined to the processes of normal burning.

36. Relation of Specific Heats at Constant Pressure: Before Combustion $(C'(p))$, after $(C''(p))$.— Consider a gaseous combustible mixture at temperature T'_0 . If the temperature of combustion of the mixture is determined at constant pressure, its temperature becomes T''_0 , the heat liberated by combustion being $Q_0(p)$ (heat combustion).

If, before the heat of combustion is determined, the temperature of the mixture be raised to T' , the temperature after combustion will be T'' .

From the relation between the initial and final state of the gases we have the relation

$$Q_0(p) = \int_{T'_0}^{T''_0} C''(p) dT = \int_{T'_0}^{T''} C''(p) dT - \int_{T'_0}^{T'} C'(p) dT.$$

The second equation may be written

$$\int_{T''_0}^{T''} C''(p) dT = \int_{T'_0}^{T'} C'(p) dT$$

On the assumption that the specific heats remain constant, we would have

$$C''(p) (T'' - T''_o) = C'(p) (T' - T'_o),$$

which may be written

$$C''(p) T'' - C'(p) T' = C''(p) T''_o - C'(p) T'_o = K \quad (1)$$

This is a relation between initial temperature and the temperature of combustion at constant pressure.

37. The Relation between the Fraction of the Fuel Burned and the Pressure.— Let $x = \frac{m}{M}$, m being the mass of the mixture burned up to the instant considered.

x will vary between 0 and 1 as m varies between 0 and M .

Since $m = Mx$, the mass of the elementary section occupying the front of the flame will be $dm = M dx$.

Its volume will be $v dm$, v being the specific volume of the burned gases.

We may then write

$$V = \int_0^M v dm = M \int_0^1 v dx = M v_m, \quad (2)$$

v_m = mean specific or initial volume.

In the gases not yet burned, we would have

$$p^{1/\gamma} v' = F' = p_o^{1/\gamma} v_m, \quad F' = \text{constant.}$$

In the burned gases this adiabatic function will not remain constant. It is a function of x :

$$p^{1/\gamma''} v'' = F''(x).$$

Corresponding magnitudes are indicated by accents. One accent stands for unburned gases, two accents for burned gases.

It may be assumed that the combustion of an elementary section takes place at constant pressure. By application of equation (1) we may then write

$$C'' T'' - C' T' = K \quad (1)$$

T' = initial temperature of the section considered.

T'' = temperature of combustion of this section.

We know that

$$C = \frac{\gamma}{\gamma - 1} \frac{R}{J}$$

$$C T = \frac{1}{J} \frac{\gamma}{\gamma - 1} p v = \frac{1}{J} \frac{\gamma}{\gamma - 1} p^{1-\frac{1}{\gamma}} F.$$

Equation (1) then becomes

$$\frac{\gamma''}{\gamma'' - 1} p^{1-\frac{1}{\gamma''}} F''(x) - \frac{\gamma'}{\gamma' - 1} p^{1-\frac{1}{\gamma'}} F' = K J$$

from which

$$F''(x) = \frac{\gamma'' - 1}{\gamma''} p^{\frac{1}{\gamma''}-1} \left(K J + \frac{\gamma'}{\gamma' - 1} p^{1-\frac{1}{\gamma'}} F' \right) \quad (5)$$

This is a relation between the value of F'' and the corresponding pressure p

Let us seek a relation between p and x .

Equations (3) and (4) give

$$v' = p^{-\frac{1}{\gamma'}} F' \quad v'' = p^{-\frac{1}{\gamma''}} F''(x).$$

Equation (2) may be written in the form of

$$\int_0^1 v \, dx = \int_0^x v'' \, dx + \int_x^1 v' \, dx = v_m.$$

If v'' and v' are replaced in this equation by their values given above

$$p^{-1/\gamma''} \int_0^x F''(x) \, dx + p^{-1/\gamma'} F' \int_x^1 dx = v_m$$

from which

$$\int_0^x F''(x) \, dx = v_m p^{1/\gamma''} - F' p^{\frac{1}{\gamma''} - \frac{1}{\gamma'}} (1 - x),$$

By differentiating in respect to x , we have

$$F''(x) = F' p^{\frac{1}{\gamma''} - \frac{1}{\gamma'}} + \left[\frac{1}{\gamma''} v_m p^{\frac{1}{\gamma''} - 1} - \left(\frac{1}{\gamma''} - \frac{1}{\gamma'} \right) F' p^{\frac{1}{\gamma''} - \frac{1}{\gamma'} - 1} (1 - x) \right] \frac{dp}{dx} \quad (6)$$

This equation may not be integrated, but if it is considered in view of the relation expressed in (5), we have

$$(\gamma'' - 1) KJ = \frac{\gamma'' - \gamma'}{\gamma' - 1} F' p^{1 - \frac{1}{\gamma'}} + \left[v_m + \frac{\gamma'' - \gamma'}{\gamma'} F' p^{-\frac{1}{\gamma'}} (1 - x) \right] \frac{dp}{dx} \quad (7)$$

This is a relation between x , p and $\frac{dp}{dx}$ and may be written

$$(\gamma'' - 1) KJ = v_m \frac{dp}{dx} + \frac{\gamma'' - \gamma'}{\gamma' - 1} F' \frac{d}{dx} \left[p^{1 - \frac{1}{\gamma'}} (1 - x) \right].$$

Integrating between x and 1

$$(\gamma'' - 1) KJ (1 - x) = v_m (p_1 - p) - \frac{\gamma'' - \gamma'}{\gamma' - 1} F' p^{1 - \frac{1}{\gamma'}} (1 - x).$$

For $x = 0$, $p = p_0$:

$$p_1 = p_0 + \frac{1}{v_m} \left[\frac{\gamma'' - \gamma'}{\gamma' - 1} F' p_0^{1 - \frac{1}{\gamma'}} + (\gamma'' - 1) KJ \right]. \quad (8)$$

Substituting this value in the preceding relation, we have

$$(1 - x) = \frac{v_m (p_1 - p)}{\frac{\gamma'' - \gamma'}{\gamma' - 1} F' p_1^{1 - \frac{1}{\gamma'}} + (\gamma'' - 1) KJ} \quad (9)$$

This is the relation sought between p and x .

Let $\pi = \frac{p}{p_0}$, then $\pi_1 = \frac{p_1}{p_0}$, and recall that

$$F' = p_0^{1/\gamma''} v_m$$

$$\text{Let } H = \frac{KJ}{R'} = \frac{K M' J}{R}$$

where M' is the molecular weight of the mixture,

R is the gas constant,

R' is the gas constant referred to 1 gram.

Then

$$\pi_1 = \frac{\gamma'' - 1}{\gamma' - 1} + (\gamma'' - 1) \frac{H}{T_0} \quad (10)$$

and

$$(1 - x) = \frac{\pi_1 - \pi}{\frac{\gamma'' - \gamma'}{\gamma' - 1} \pi^{1 - \frac{1}{\gamma'}} + (\gamma'' - 1) \frac{H}{T_0}} \quad (11)$$

Let us designate by V_X the volume occupied by the burned gas at the instant the fraction x of the unburned gas is entering the combustion zone. Then from the preceding (2) we may write

$$V - V_X = M \int_x^1 v' dx \quad \text{with} \quad v' = \pi^{-\frac{1}{\gamma'}} v_m$$

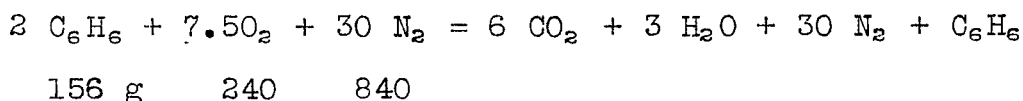
$$V - V_X = M v' (1 - x) = M v_m \pi^{-\frac{1}{\gamma'}} (1 - x) = V \pi^{-\frac{1}{\gamma'}} (1 - x),$$

from which according to (11)

$$V_x = V \left[1 - \pi^{-1/\gamma'} \frac{\pi_0 - \pi}{\frac{\gamma'' - \gamma'}{\gamma' - 1} \pi^{1 - \frac{1}{\gamma'}} + (\gamma'' - 1) \frac{H}{T_0}} \right] \quad (12)$$

We shall not attempt to apply formulas (10), (11), and (12) in order to obtain in the particular case of the combustion of a mixture of benzene and air, the value of π_1 and the way π varies as a function of x .

38. Calculation of K.— Consider the following reaction:



(A mixture is selected of the same composition as that for which the velocity of propagation has been determined.)

The initial temperature of the mixture is T'_0 . If the reaction was initiated at this temperature, then the temperature attained would be T''_0 . But since the mixture is heated before ignition, the final temperature will be designated by T''_1 .

We have seen from the preceding that

$$Q_0(p) = C'' T''_0 - C' T'_0$$

($Q(p)$ is the heat of combustion at constant pressure.)

$$C'' T''_1 - C' T'_1 = C'' T''_0 - C' T'_0 = K$$

from which

$$K = Q_0(p) - (C' - C'') T'_0.$$

We take for the heat of combustion of benzene, 9545 cal per g.

For one gram of the explosive mixture there will be

$\frac{78}{1236} = 0.0630$ grams of benzene burned. This will produce
 $Q_0(p) = 0.063 \times 9545 = 603$ calories.

The specific heat of the mixture is given by

$$C = \frac{\sum m C}{\sum m}$$

For C' at $T'_0 = 273^\circ$, we take for

O_2	0.2056	(Holborn u. Henning)
N_2	0.2350	-- --
C_6H_6	0.375	(Aubert, vapor between 120 & 220).

We shall calculate C'' at 2000° by Pier's formula, which is applicable to 2000° .

N_2	$0.2459 + 16.1 \times 10^{-6} \times 2000$	0.278
CO_2	$0.1997 + 75 \times 10^{-6} \times 2000 - 21.6 \times 10^{-9} \times 2000^2$	0.281
H_2O	$0.4472 + 27.8 \times 10^{-6} \times 2000 - 11.1 \times 10^{-12} \times 2000^3$	0.592
C_6H_6	(No precise value known, we take)	0.400

From these values we have calculated the specific heats of

$$C' = 0.255 \qquad C'' = 0.300$$

from which we find

$$K = 603 + (0.300 - 0.255) \times 273 = 591 \text{ calories.}$$

39. Calculation of H , γ' , γ'' . -- We have taken the relation

$$H = \frac{K M' J}{R}$$

M' = molecular mass of the mixture.

Substituting numerical values

$$H = \frac{591 \times 31.3 \times 4.18}{8.3} = 9330.$$

We know that

$$C = \frac{R\gamma}{JM(\gamma - 1)}$$

$$\gamma = \frac{1}{1 - \frac{R}{JCM}}$$

$$\gamma' = \frac{1}{1 - \frac{R}{JC'M'}}$$

$$\gamma'' = \frac{1}{1 - \frac{R}{JC''M''}}$$

Passing to numerical values,

$$\gamma' = 1.32$$

$$\gamma'' = 1.26$$

We are in possession now of all magnitudes necessary to satisfy formulas (10), (11), (12):

$$\gamma' = 1.32, \quad \gamma'' = 1.26, \quad H = 9330, \quad T_0 = 539$$

40. Numerical Values.— The following table gives some values calculated by the aid of formulas given above:

$\pi = \frac{p}{p_1}$	$x = \frac{m}{M}$	$\frac{Vx}{V}$
1.2	0.047	0.17
2.0	0.228	0.54
3.0	0.457	0.77
4.0	0.690	0.895
5.0	0.925	0.980
5.32 = π_1	1.000	1.000

It results from the preceding theory:

1. That the pressure in a closed tube is very nearly proportional to the mass of the mixture burned.

2. That the displacement of the flame is at first rapid as compared to the mass of mixture burned. Toward the end of burning it becomes slower while the mass burned is greater.

3. Pressure increases slowly at first as compared with flame displacement and increases rapidly toward the end of the reaction.

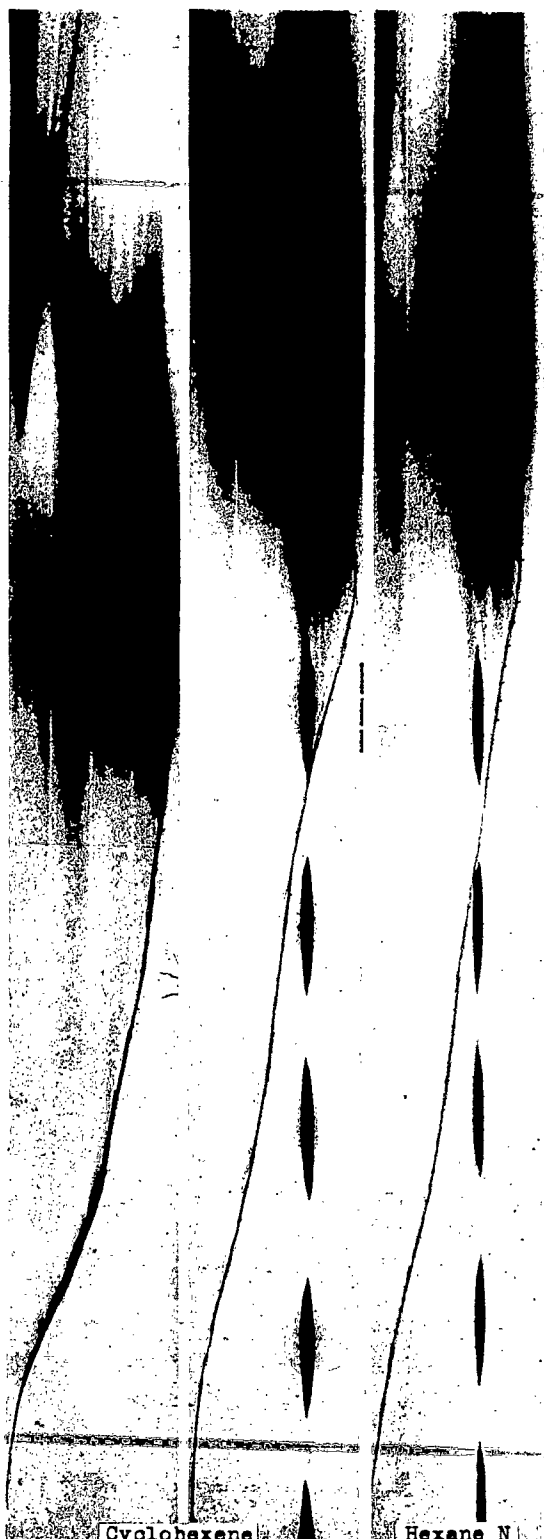
4. We have no theory to offer connecting the variation of these factors with time. The photographs obtained may in a way supply this deficiency since they show the position of the flame $\frac{Vx}{V}$ as a function of time. These records, however, we hold as incomplete since the passage of the flame does not complete the

reaction. It indicates only an unknown function of it.

41. Note.— The material presented in this paper is the result of a very incomplete study that it is our intention to continue and extend.

It is planned to use a tube as well as a lens of quartz; to make provision for further modifications in the tube's dimensions, and to study other gaseous mixtures.

In closing, we wish to express our gratitude and obligation to all those who have assisted in any way, but especially our acknowledgments are due to Professors Cotton and Jouguet, who have given us many valuable suggestions.



Cyclohexene
Photo. 1
 $c = 17.7$
 $r = 4.5$
Photo. 2
 $c = 20.0$
 $r = 4.5$
PLATE I

Hexane N
Photo. 3
 $c = 10.7$
 $r = 4.5$

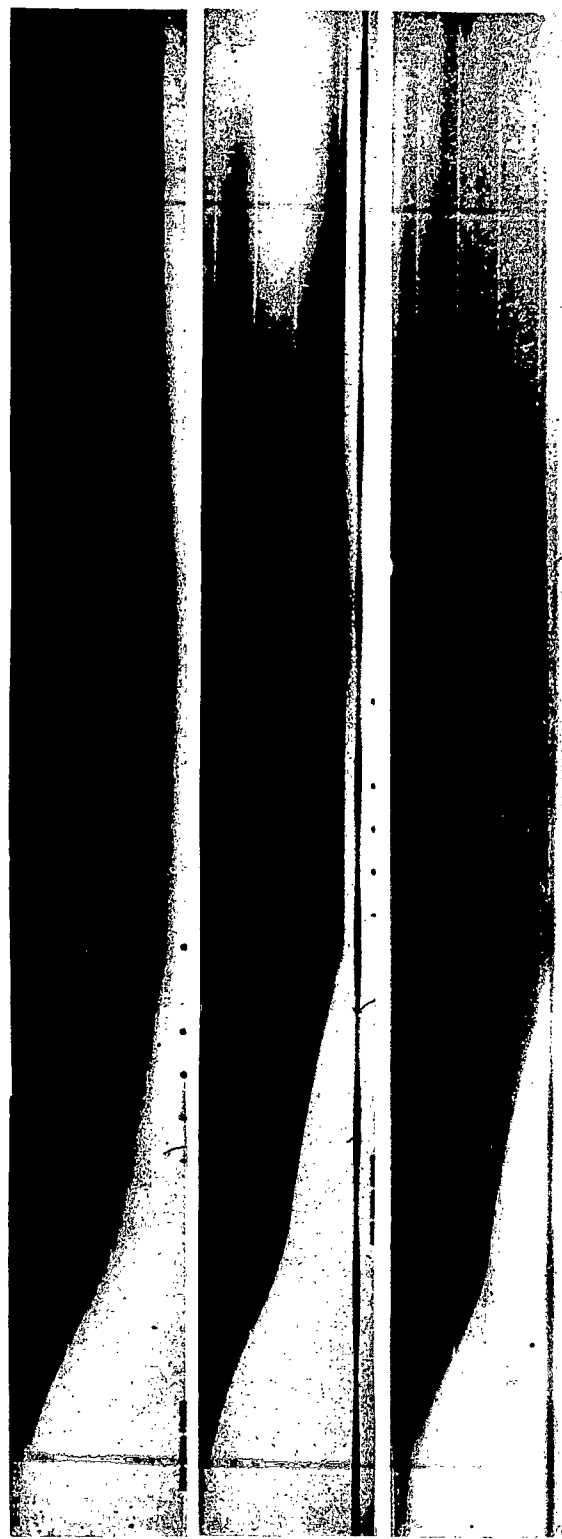


Photo. 1
 $t_o = 55^\circ$

Photo. 2
 $t_o = 70^\circ$

Photo. 3
 $t_o = 85^\circ$

PLATE II. Photos obtained with same mixture of benzine and air. $c = 0.14$, $r = 5$.
14954 A.S.

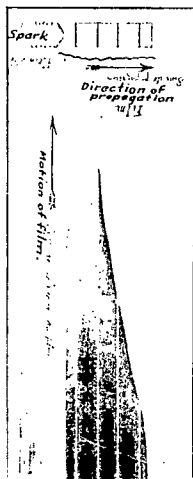


FIG. 11

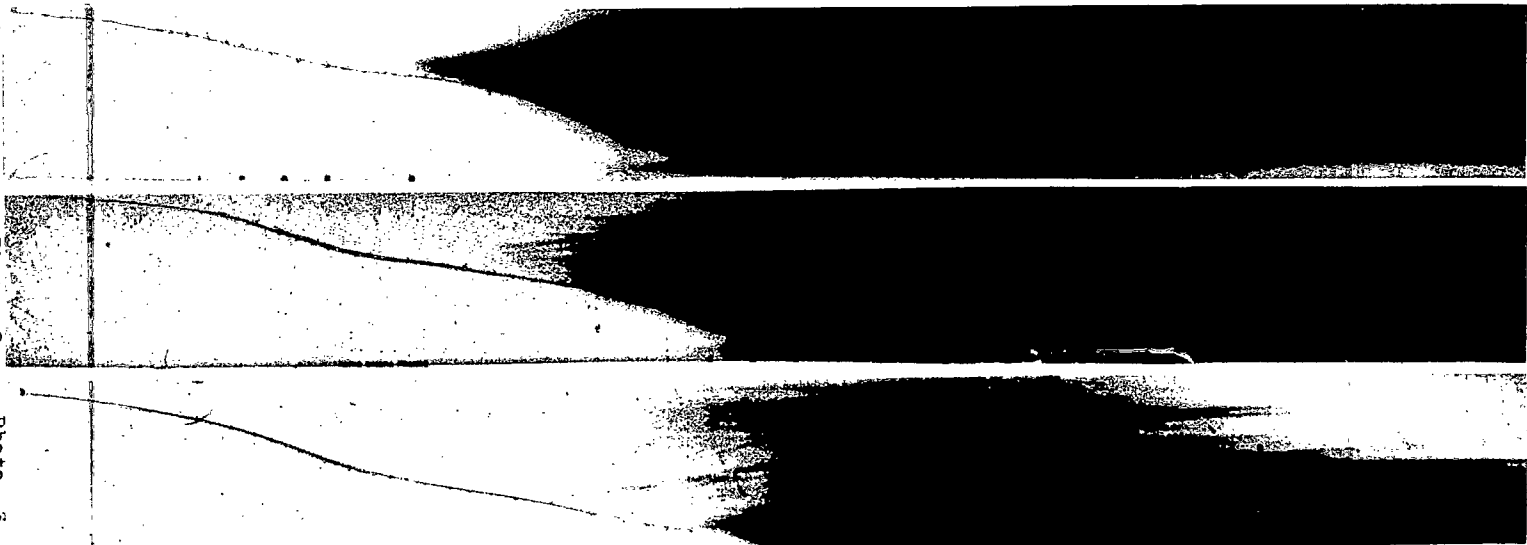


Photo. 1
Without t-c.1
PLATE III

Photo. 2
1% t-c.1

Cyclohexene,
tetra-ethyl lead.

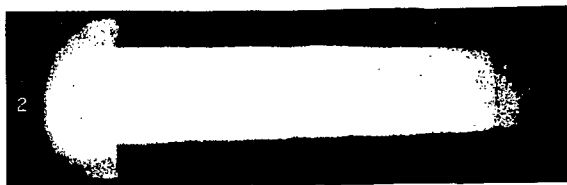
Photo. 3
2% t-c.1

Effect of

PLATE IV
Flame front
traversed
whole tube
before
explosion.



1 Impression on fixed photo plate
during deflagration of mixture
with 12.8% hexane



2 Photograph under same conditions
as No. 1 but with hexane contain-
ing 5% tetra-ethyl lead.

Fig. 20b Photographs taken during deflagration of mixture.

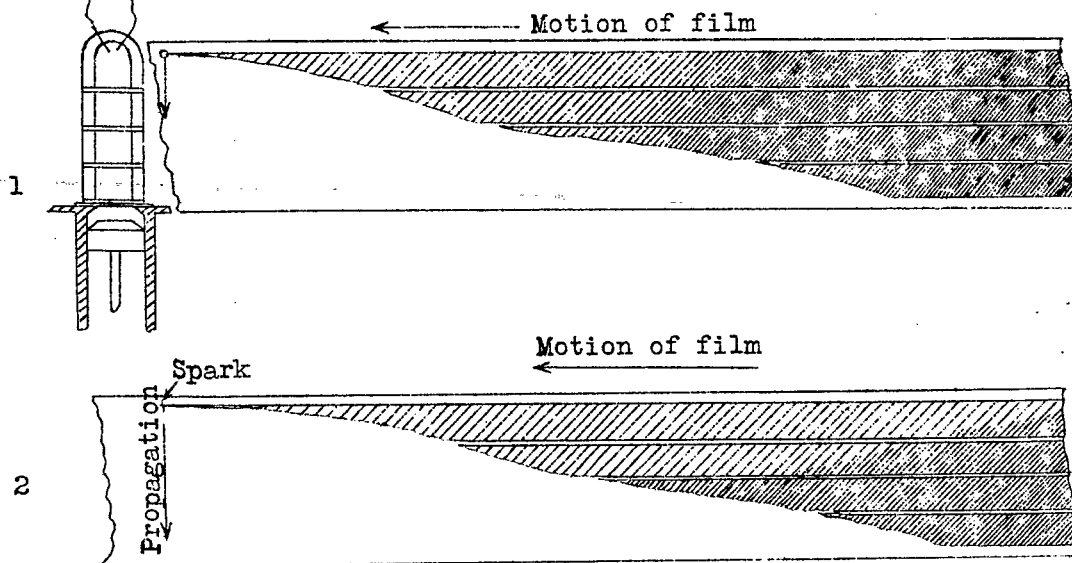


Fig.12

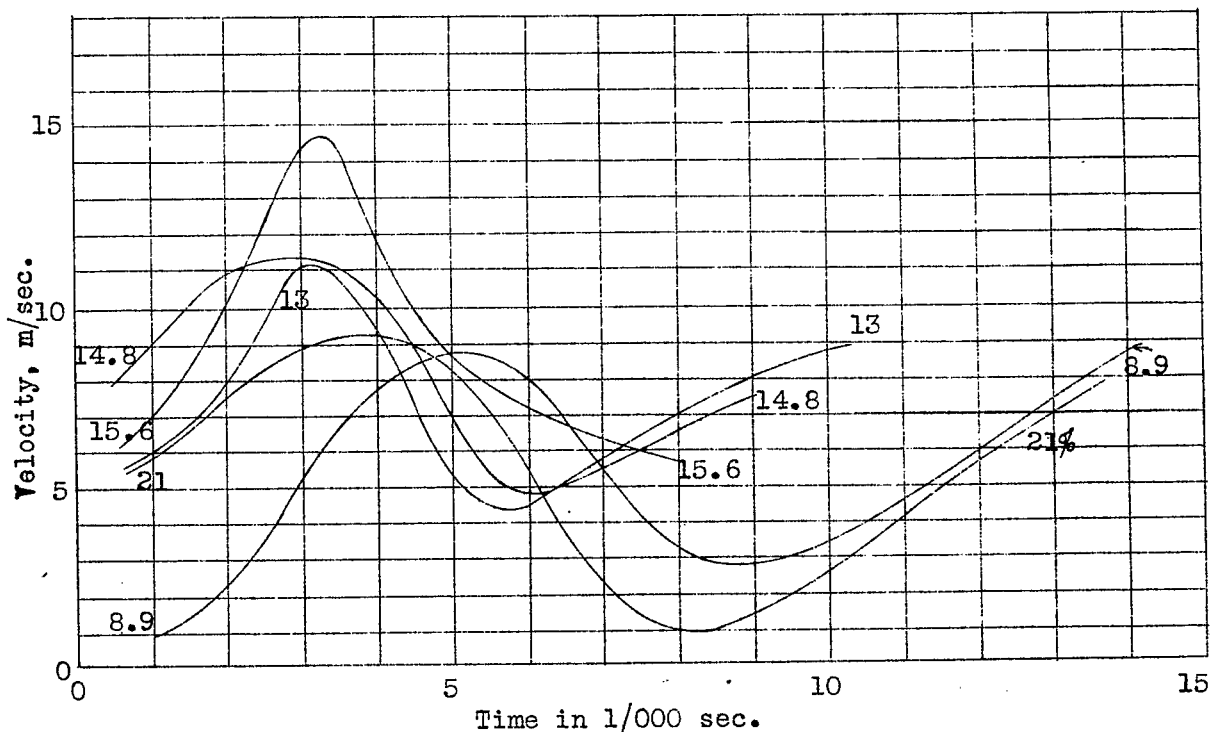


Fig.13 Curves showing variable velocity of flame front with time for different mixture ratios. (Benzène)

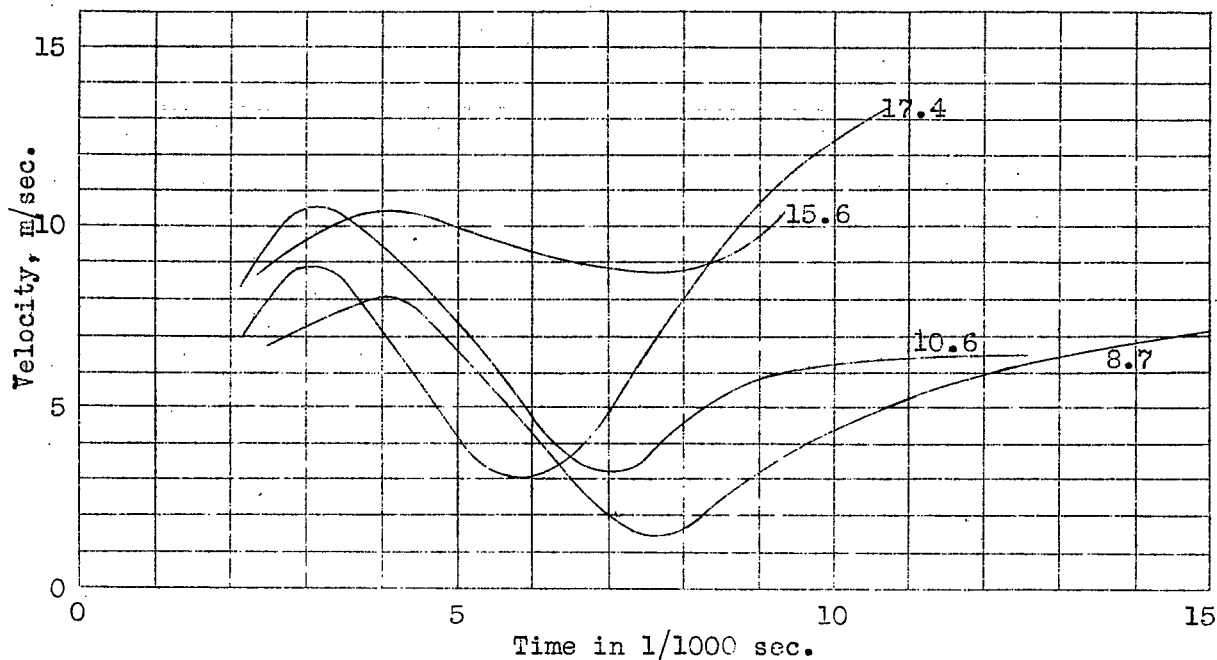


Fig.14 Curves showing variable velocity of flame front with time for different mixture ratios. (Cyclohexane)

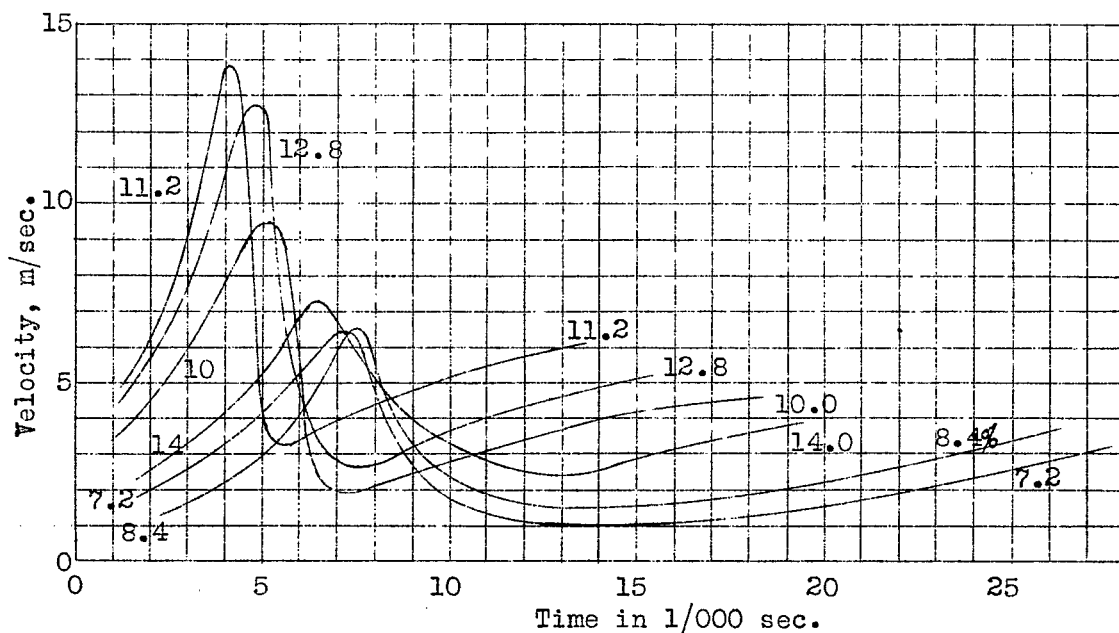


Fig.15 Curves showing variable velocity of flame front with time for different mixture ratios. (Cyclohexane)

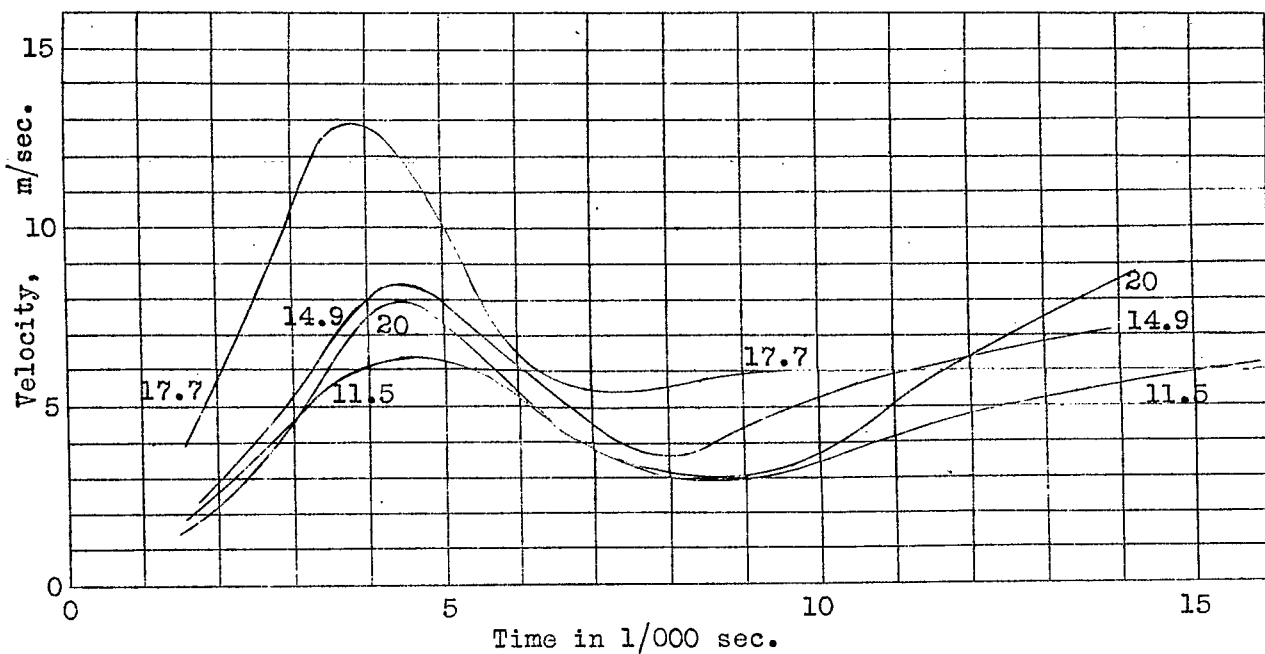


Fig.16 Curves showing variable velocity of flame front with time for different mixture ratios. (Cyclohexène)

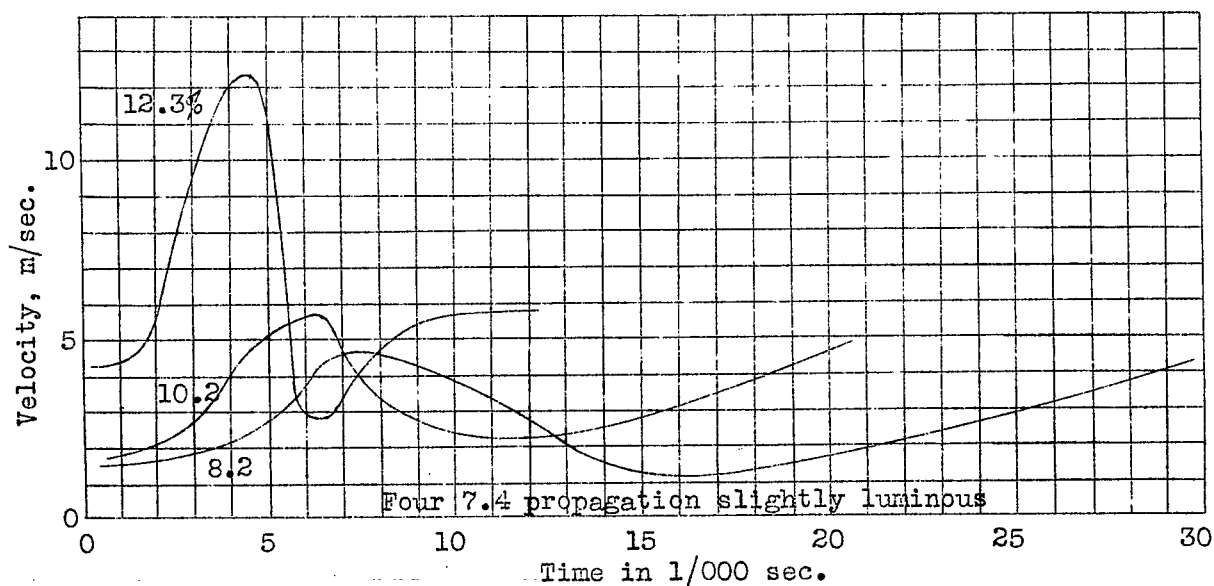


Fig.17 Curves showing variable velocity of flame front with time for different mixture ratios. (Cyclohexène)

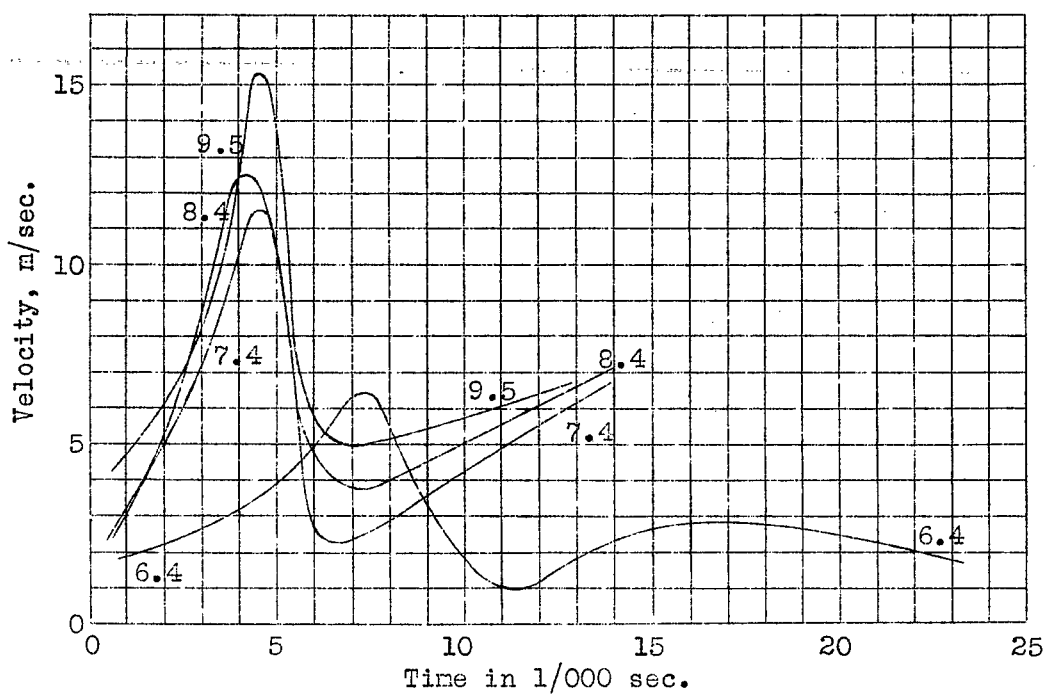


Fig.18 Curves showing variable velocity of flame front with time for different mixture ratios. (Hexane N)

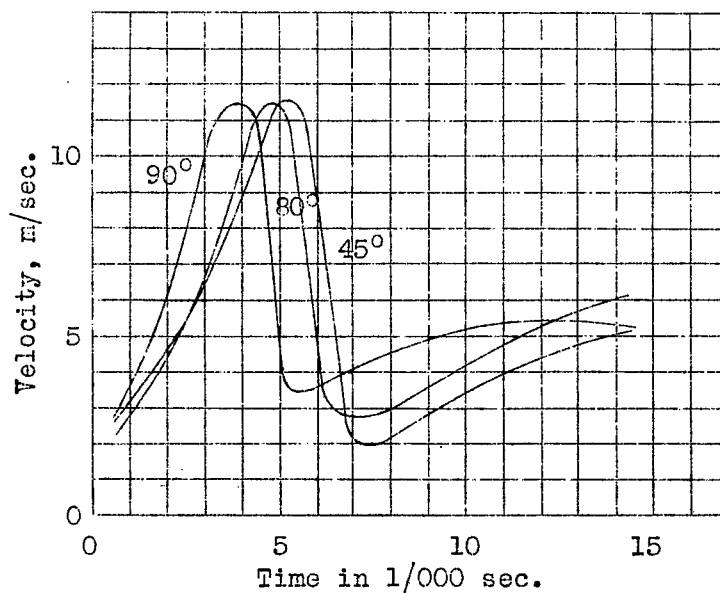


Fig.19 Curves showing variable velocity of flame front for different initial temperatures. (Hexane)

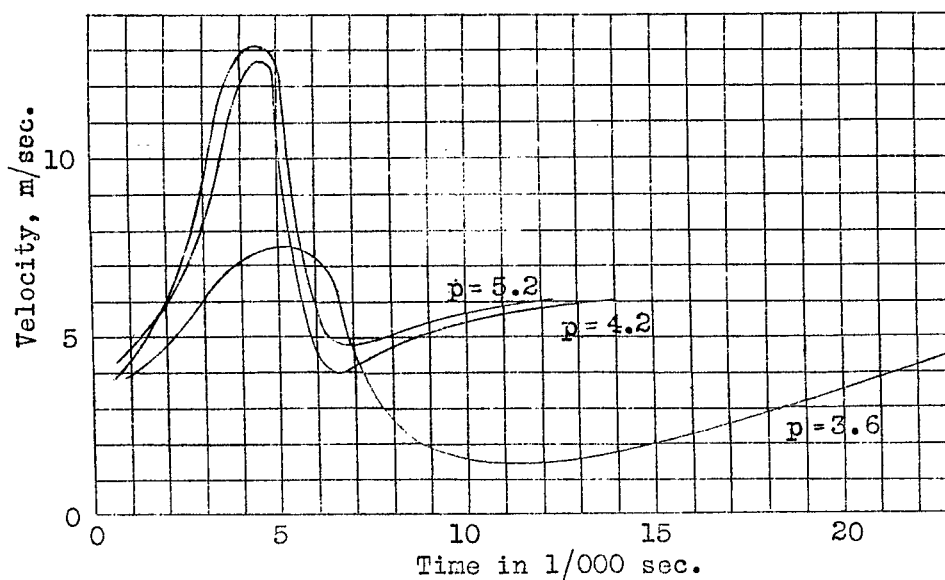


Fig.20 Effect of compression ratio $r = V/v$ richness of mixture, 15%.

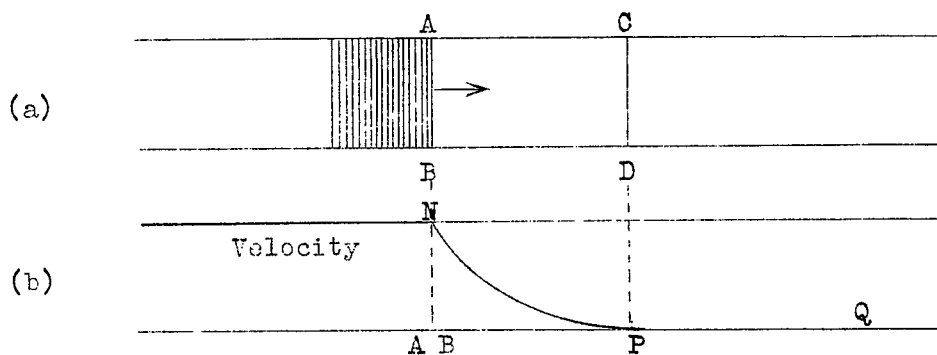


Fig.21

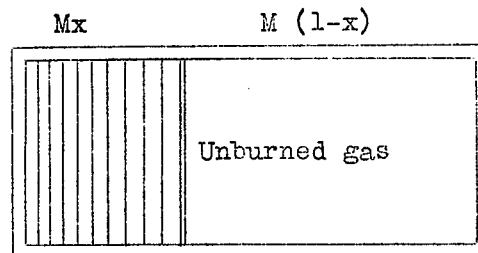


Fig.22

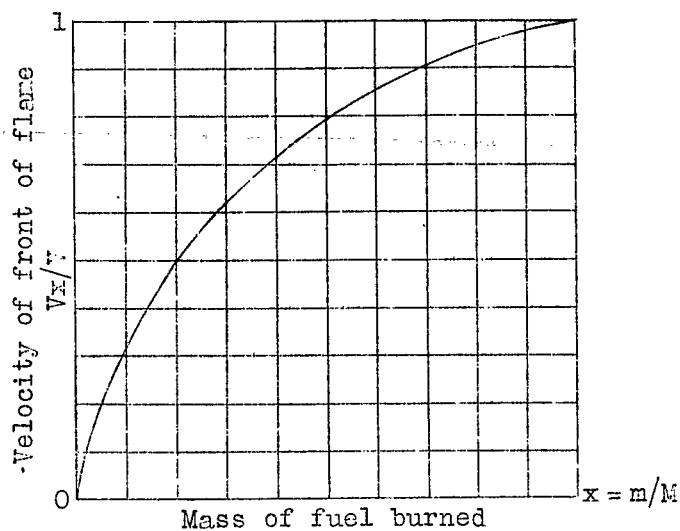


Fig.23 Flame displacement relative to mass of fuel burned.

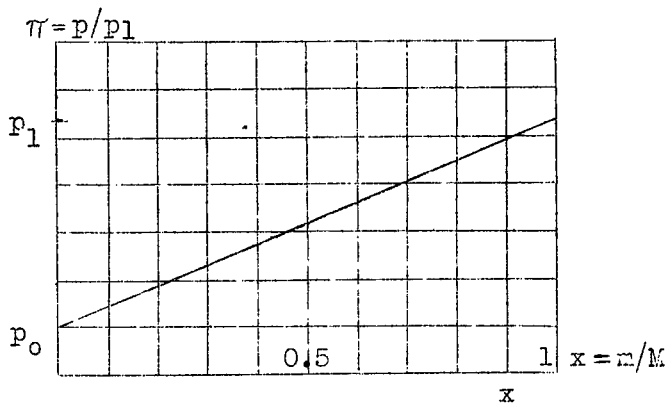


Fig.24 Increase of pressure relative to mass of fuel burned.

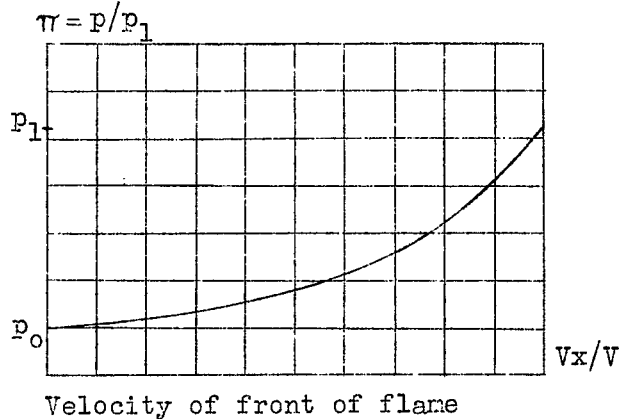


Fig.25 Increase of pressure relative to position of flame in tube.

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